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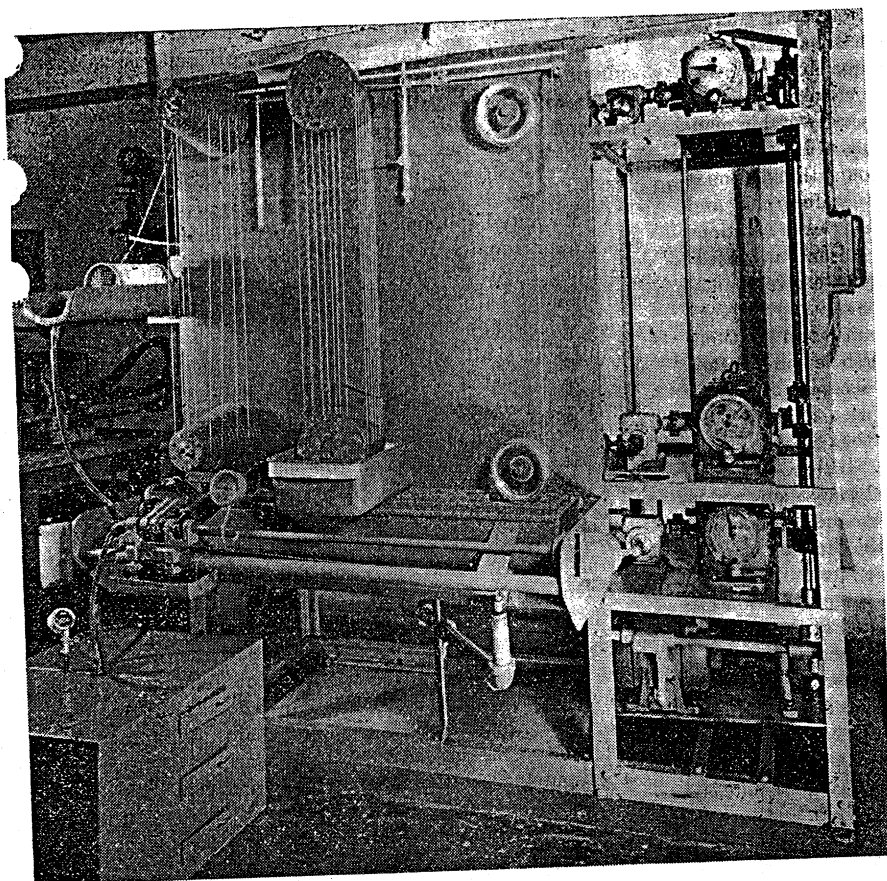


Figure 1. Spinning Apparatus

**TEXTILE**

**FIBER**

**from**

**CASEIN**

## Factors Affecting the Tensile Strength

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**T**HE casein fiber, Aralac, is being manufactured in the United States at the rate of several million pounds a year. The material is used as a textile fiber and is also blended with imported rabbit fur in making hats (3, 22). Despite the fluctuation of the market price of casein from 15 to 30 cents a pound, quotations on the manufactured textile fiber have not varied from 64 cents a pound in recent years. The economic position of casein fiber in various countries has been favorably discussed by several authors (2, 11, 15). Artificial protein fibers have been made from soybean, peanut, and other proteins by essentially the same process employed for casein: solution of the protein in alkali, extrusion of the solution into a precipitating bath containing acid and salt, and hardening of the fiber with formaldehyde (6, 9). Expansion of the casein fiber industry and large-scale production of similar fibers from other proteins will depend in a postwar economy on relative price and relative quality. Further development of the wet and dry strengths will enhance the competitive position of this class of fibers.

Although large-scale commercial development of casein fiber started in Italy in 1936, processes were invented for manufacturing casein fiber prior to that date. In 1899 two patents (21)

were issued to Millar covering manufacture of a casein fiber by spinning into air. A 50% solution of casein in glacial acetic acid was used. Shortly afterward, Todtenhaupt was granted a series of four German patents (23). Present-day methods for spinning alkaline solutions of proteins represent refinements of this early work. In 1936 the manufacture of casein fiber, known as Lanital, was begun by Snia Viscosa in Italy, under the Ferretti patents (10). Working independently in this country, Whittier and Gould obtained eight public service patents (29) on the production of casein fibers.

Todtenhaupt's fibers tended to stick together and were hard and brittle (17, 26). Ferretti's patents emphasized the use of a special "textile" casein in overcoming these difficulties. Ferretti also incorporates aluminum salts in the spinning bath as well as salt in the formaldehyde hardening bath. Certainly improvements in machinery for spinning fiber achieved by the rayon industry between 1904 and 1936 were an important factor in the development and production of Lanital fiber. Ferretti's British Patent 483,731 covers in detail a process for manufacturing casein fiber. The special textile casein is prepared from skim milk by precipitation with sulfuric acid in 56% excess of the amount or-

dinarily employed to coagulate the casein. The casein is heated with the acid whey at a pH of 2.9 to 3.0 for one hour at 45° C. The curd is separated and pressed to remove the serum content and dried without washing. This special casein is made into solution, using a quantity of sodium hydroxide equal to 9.76 grams per 100 grams of moisture-free casein. As the viscosity increases with age, the solution is diluted to keep the viscosity within manageable limits. The final concentration in terms of moisture-free casein is 16 to 18%. After being aged for 48 hours, the solution is spun into a precipitating bath of sodium sulfate, sulfuric acid, and aluminum sulfate. The fiber is hardened in a series of solutions containing sodium chloride and formaldehyde, washed, and dried.

Küntzel and Doehner (18) reported the only extensive quantitative data dealing with the effect of spinning conditions and materials on filament strength. These authors spun casein solutions with a viscosity of 4 to 6 poises through single-hole spinnerettes into a bath held at 52° C. In our experience these conditions of temperature and viscosity are satisfactory with a single-hole spinnerette, but owing to formation of blebs they are not satisfactory with multihole spinnerettes. However, their conclusions are of considerable interest especially in regard to a salient point of the Ferretti patents. According to them, the only advantage in use of excess sulfuric acid in precipitating the "textile" casein is the subsequent introduction of sodium sulfate into the spinning solution. Better results are claimed for the direct addition of sodium sulfate to a solution of casein precipitated at the isoelectric point. Their casein fibers gave an x-ray diagram which showed no orientation, even when the fibers were stretched.

The patents issued to Whittier and Gould (29) are concerned mainly with the additions of various agents to the casein solution or to the precipitating bath for the purpose of modifying the resulting fiber. For example, in the first patent sodium aluminate is employed in the spinning solution to increase strength and water resistance, and fat acids, to improve flexibility and softness. Another patent describes the spinning of fibers from concentrated skim milk. They used a ratio of sodium hydroxide to casein lower than Ferretti's to minimize hydrolysis of the casein. The solutions, prepared from any acid-precipitated casein of good quality, are spun without aging.

Patents recently issued to Atwood (5) reveal in detail processes for the production of casein fiber. Some features are (a) very low alkalinity of spinning solution, corresponding to a pH of 7 and about 2 grams of sodium hydroxide per 100 grams of casein, (b) a short procedure for dispersing acid or rennet casein with the aid of heat, (c) a continuous method for treating with formaldehyde, and (d) acetylation with ketene or acetic anhydride.

It is obvious that, whereas a great deal has been accomplished in the development of artificial protein fiber, much remains to be done. Acetylation has provided a means for making such fiber resistant to boiling aqueous solution. Eventual enhancement of all the basic properties within limits of compatibility is desired. These properties are, of course, considerably interdependent. It

is generally agreed, however, that the current need is for higher wet and dry strengths. This study was undertaken to evaluate some of the factors contributing to the strength of casein fiber. The principal factors investigated were pH and viscosity of the spinning solution, composition of the precipitating bath, effects of drawoff and godet stretch, and progressive stretch during hardening.

#### APPARATUS AND METHODS

A substantial spinning machine was constructed with a steel frame approximately 6 × 6 × 2 feet to hold the various reduction gears and drives (Figure 1). The metering gear pump assembly and spinning bath are located on the front of the frame. Glass godet wheels (wheels for guiding or stretching the yarn) are mounted on shaft extensions above the precipitating bath. A large panel coated with acid-resisting paint serves as a splash shield. A two-horsepower, 1725 r.p.m. motor is coupled to a vertical countershaft through a worm and pinion reduction gear. By means of spiral miter gears this shaft energizes three variable-ratio (nonslip) chain drives, placed vertically above one another in the frame. Three reduction units couple the variable drives to three drive shafts on the machine. The lowest variable drive thus controls the gear pump for the casein solution; the middle variable drive controls the speed of the first godet (take-off wheel); and the upper variable drive controls the speed of the other godet wheels and the traversing reel which collects the fiber. This reel has a unique feature, in that the fiber tow remains in the same relative position while the bobbin is moved back and forth by the traversing mechanism. By changing chains and sprockets, any set of godet wheels may be run from any variable drive.

The spinning solution is contained in a converted 27-quart pressure cooker enclosed in a wooden cover. Air pressure lifts the viscous material to the metering pump, which forces it at a uniform rate through a standard viscose candle filter and thence through the glass gooseneck to the spinnerette. A gage registers the pressure in the line between the gear pump and the filter. The pressure ordinarily stood at 150 pounds per square inch for a viscosity of 200 poises at 25° C. A multihole spinnerette was used so that moderate amounts of fiber could be spun and the results would be applicable to commercial practice. The same spinnerette, a platinum-gold alloy cup with a 1.5-inch diameter face containing two hundred and fifty 0.003-inch holes arranged in concentric circles, was used in the experiments reported here. The precipitating bath was contained in a rubber-lined trough, 8 inches wide, 8 inches deep, and 40 inches long. Two precipitating baths differing with regard to the incorporation of aluminum salt were employed:

PRECIPITATING BATH I	PRECIPITATING BATH II
5500 cc. H <sub>2</sub> O	5500 cc. H <sub>2</sub> O
1200 grams Na <sub>2</sub> SO <sub>4</sub>	1800 grams Na <sub>2</sub> SO <sub>4</sub>
600 grams Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·18H <sub>2</sub> O	810 grams concd. H <sub>2</sub> SO <sub>4</sub>
810 grams concd. H <sub>2</sub> SO <sub>4</sub>	

Studies on the preparation of fibers from acid-precipitated casein with a laboratory spinning machine are reported. Attention was directed to the major operations of fiber production—namely, dissolving the casein, spinning, stretching, and hardening. A spinning solution containing 20% protein and having a pH of 9.2 was employed in most of the experiments. All fibers were given a final hardening treatment with formaldehyde. Stretching the tow issuing from the spinnerette, either in the precipitating bath or between godet wheels in air, gave a tensile strength of about 0.7 gram per denier. Under these conditions of stretching, the addition of aluminum sulfate to the precipitating bath containing sulfuric acid and sodium sulfate did not affect the strength of the fiber. However, such incorporation of aluminum sulfate had a marked effect in a subsequent operation involving simultaneous stretching and partial hardening with formaldehyde. When the latter process was operated at 85° C., a dry strength of 1 gram per denier and a wet strength of 0.5 gram per denier were obtained. Comparative measurements of tensile strength of artificial protein fibers which will be exposed to moisture are best made after the fibers have been swollen in water and dried.

The baths as well as the spinning solutions were at room temperature, 25° to 28° C. The concentration of acid in the bath was permitted to decrease more than 5% of the total during an experiment.

After traveling about 20 inches in the spinning bath, the tow of filaments from the spinnerette is gathered by the first godet wheel on the lower right, passes over the second wheel mounted immediately above it, and then proceeds to the bobbin. (When a skein required, the tow is passed in an endless loop around two godet wheels until sufficient fiber has been accumulated.) Early experiments indicated that stretching treatments were much more effective if the fiber was under tension during the formaldehyde hardening.

Consequently the fiber was hardened on bobbins. To neutralize the acid carried over from the highly acid precipitating baths, a strongly buffered hardening bath was used. It consisted of 30% sodium acetate and 5% formaldehyde, adjusted to pH 5.8 by addition of acetic acid. For convenience, hardening was done overnight (16 hours), but less time would suffice. The fiber was finally washed for 8 hours in running water, dried for 24 hours at room temperature, cut from the bobbins, treated to remove stresses, and then tested.

TABLE I. EFFECT OF pH OF CASEIN SOLUTION ON TENSILE STRENGTH OF FIBER

(Solutions held at 25° C. for 24 hours; pump rates varied to give fiber of same denier; precipitating bath I at 25-28° C.; drawoff rate, 17.9 meters per min., godet stretch, 41%)

pH of Casein Soln.	NaOH, G./100 G. Casein	Casein, %	Viscosity, Poises (25° C.)	Tensile Strength, G./Denier		
				70° F., 65% r.h.	Wet	Ratio, wet to dry
10.40	6.84	24.8	144	0.51	0.11	0.22
9.21	4.00	19.6	200	0.65	0.24	0.37
6.65	2.66	20.0	200	0.62	0.29	0.47

When the fiber was dried on bobbins, it tended to contract with considerable force. Cutting across the fibers sometimes released the tension with an audible snap. The cut, dry fiber was still subject to residual strains, as shown by contraction in length upon immersion in water. Heim (13) has shown that stretched casein fiber contracts to its original length rapidly in water but very slowly when dry. These and other observations led to the suspicion that unrelaxed fibers would evince excess tensile strength, and this was found to be the case. For example, the tensile strength of one sample of highly stretched fiber, dried on the bobbin, was 1 gram per denier. However, when the fiber was cut from the bobbin, wet, and dried before testing, the tensile strength dropped to 0.85 gram per denier and remained at that figure even after another wetting and drying. One factor involved in the higher tensile value is its calculation on the basis of a transiently reduced cross section. The higher strength is dissipated rapidly by water but slowly by the moisture of the atmosphere. Therefore, a practical basis for evaluation of the tensile strength is the value obtained after the fiber is swelled in water and dried without tension. All the results reported here were obtained by this procedure.

Tensile strength was measured with a Scott I P-2 serigraph. Determinations were first made with the spark-recording attachment on single fibers, but the large spread in the values required forty to fifty tests to yield an average of sufficient accuracy. In addition, the circulating air of the testing room dried out wet single fibers so rapidly that erroneous figures for wet strength resulted. For these reasons, a modified bundle test was adopted. As expected, results obtained with the bundle test were less than averages of single fiber tests, usually about 15% lower. The procedure was based on the A.S.T.M. method for rayon staple (1). The needle combs and general technique of handling the fiber specified under D540-41T are employed, but smaller bundles broken on a machine of smaller capacity.

The test bundles are prepared as follows: About a 2-inch sec-

tion of tow material is cut. Held in the fingers, this is passed through the fine comb ten times, starting near the ends of the fibers, and proceeding by stages to the center of the bundle. The bundle is then shifted, and the other half combed in the same fashion. The parallel fibers are laid on a cutting block and held down by a brass template 22.5 mm. wide; a razor blade is used to sever the protruding ends. The fiber bundle is now weighed to 0.01 mg. on a microtorsion balance with a capacity of 0 to 10 mg. Only bundles falling in the range 2.00 to 2.75 mg. are used. Two pieces of masking tape, 1 inch long and 1/2 inch wide, are laid with their adhesive faces up and their long sides parallel. They are held about 1/16 inch apart by temporary attachment to a card. The fiber bundle is laid on the strips and the fiber is carefully pressed into the adhesive. The ends of the tape are brought over to cover the adhesive surface, and the bundle is marked with its weight.

The flat bundles described above are broken on the testing machine with the jaws set 1 mm. apart. Since an extension is necessary to place the jaws at this distance, a small correction factor is applied for the increase in weight of the carriage. Load is applied at the rate of 1.0 to 1.4 grams per denier per minute, depending on variations in the weight of the bundle. The bundles are broken at 70° F. and 65% relative humidity in the testing room after the fiber has been equilibrated at these conditions overnight (16 hours). The results of ten bundle tests are averaged in each evaluation. Statistical appraisal of several such series of ten from different fiber preparations showed the following characteristics: Standard deviation, 0.03 gram per denier; standard deviation of the mean (of ten bundle tests), 0.0096; standard deviation of the difference of two such means, 0.0133. Therefore, differences in strength amounting to 0.03 gram per denier may be regarded as significant. Wet strengths are obtained by the same procedure except that the taped bundles are placed in distilled water for 30 minutes before they are broken. The film of water retained by the bundle prevents drying of the fibers while they are tested.

TABLE II. COMPOSITION OF CASEIN<sup>a</sup> AND CASEIN FIBER (Casein solution at pH 9.2; held at 55° C. for 16 hours and spun into bath I)

	Casein, % <sup>b</sup>	Fiber, % <sup>b</sup>
Carbon	49.13	51.00
Hydrogen	7.48	7.68
Nitrogen	14.80	14.02
Ash	1.88	2.10
Ash, Ca(Ac) <sub>2</sub> method	2.70	4.97
Phosphorus	0.86	0.74
Sulfur	0.79	1.14
Aluminum	Trace	0.50
Formaldehyde	None	2.03

<sup>a</sup> This analysis is representative of the commercial product, a low-ash casein precipitated with hydrochloric acid, which was used in all the experiments.

<sup>b</sup> Moisture-free basis.

#### EFFECT OF ALKALI

It appeared important first to investigate the influence on fiber strength of spinning solutions having a lower alkali content than that proposed by Ferretti. As already pointed out (5, 29), such solutions of lower pH have been employed and have been claimed to yield increased strength (14). We attempted to spin a series of solutions with a uniform 20% concentration but with pH ranging from 7 to 10.5. However, the solution of highest pH was too low in viscosity to spin from a multihole spinnerette. In this instance it was necessary to increase the concentration of casein. Three solutions of different pH were deaerated by letting them stand for 24 hours, spun into bath I containing aluminum salt, and hardened with formaldehyde as described. As Table I shows, dry and wet strengths of the fiber prepared from the spinning solution at pH 10.4 are definitely lower than the strengths of the fibers prepared from solutions at pH 9.2 and 6.7. A reasonable assumption is that cleavage of protein chains at the higher pH was

responsible for the decrease in fiber strength. It is conceivable that harmful degradation of this kind could result from scission of some peptide bonds with only small liberation of amino nitrogen. Losses of ammonia, sulfur, and phosphoric acid occur at pH 10.4 but are not necessarily associated with chain splitting.

Table II illustrates some composition changes which occur when casein is converted to fiber by the general procedure described here. In this case the pH of the spinning solution was 9.2. There is little, if any, loss of organic phosphorus. The increase in the ash reflects the uptake of 0.5% aluminum from the spinning bath. Any change in the organic sulfur of the casein is masked by the sulfate-sulfur picked up from the precipitating bath. The amount of formaldehyde introduced into the fiber by the hardening process employed in these experiments is about 2%.

TABLE III. EFFECT OF VISCOSITY OF CASEIN SOLUTION ON TENSILE STRENGTH OF FIBER

(Solutions at pH 10.8, held at 25° C. for 24 hours; pump rate constant at 21.1 cc. per min.; precipitating bath I at 25–28° C.; drawoff rate, 17.9 meters per min.; godet stretch, 41%)

Casein Solution		Tensile Strength, G./Denier		
Concn., %	Viscosity, poises (25° C.)	70° F., 65% r.h.	Wet	Ratio, wet to dry
25.5	299	0.54	0.11	0.19
24.3	170	0.57	0.11	0.19
23.0	121	0.59	0.12	0.20
22.0	67	0.57	0.11	0.19

Since it is difficult to attain exact control of viscosity in preparing spinning solutions, experiments were undertaken to determine whether viscosity of the casein solution influenced the tensile strength of the fiber. The change of viscosity with concentration is so great that we were able to attain a fourfold increase in viscosity with only a 15% increase in protein concentration. The data in Table III do not indicate any appreciable effect over the viscosity range 67 to 299 poises. The pH of the casein solutions was 10.8. The same result was secured with solutions having viscosities from 53 to 252 at pH 9.2 and from 45 to 157 at pH 7.1. The dry strength values in Table III are higher than that in Table I for the corresponding pH. This was due to the fact that different lots of casein were employed in the two sets of experiments.

#### EFFECT OF STRETCHING

Attention was next directed to evaluating the relative effects of the various stretching treatments on the strength of the finished fiber. The results are presented in Tables IV and V. For this series of experiments the spinning solution contained 20% casein and 4.5 grams of sodium hydroxide per 100 grams of dry casein. The pH was 9.2. Candle filtration alone did not ensure stable operation of the spinnerette for production of the number of samples required. Hence, the solution was supercentrifuged at 55° C. and then held at this temperature for 16 hours to dissipate the entrained air. The viscosity was 200 poises at 25° C., the temperature of the precipitating bath. The metering gear pump was set to feed 20.3 cc. of casein solution to the spinnerette per minute. The same lot of casein was employed throughout.

The first stretching operation ordinarily takes place in the precipitating bath, where the sodium caseinate solution is converted to insoluble casein by action of the acid and the newly formed filament is partially dehydrated by the action of the salts. The stretch given the fiber at this stage is dependent upon the speed at which the fiber is removed from the precipitating bath relative to the speed of extrusion. The flow of spinning solution through the spinnerette was held constant while the drawoff rate was increased tenfold by steps to 47 meters per minute. Strength progressively improved with drawoff rate until the latter reached the range of 20 to 30 meters per minute (Table IVA). Further stretch was of no benefit. The maximum strength of about 0.69 gram

per denier showed no significant dependence on aluminum salt in the precipitating bath. The next step was to determine whether godet stretch superimposed on a moderate drawoff stretch would further increase tensile strength. The results of applying godet stretch combined with a drawoff rate of 17.9 meters per minute are reported in Table IVB. The figures show that the maximum strength thus secured with the bath containing aluminum salt is slightly greater than the corresponding maximum strength obtained by maximum drawoff stretch alone (Table IVA). Under the experimental conditions, strength from both types of stretch appeared to approach the same limit.

Application of stretch in the manner described above entails drawing of a weak and water-laden fiber, which is only subsequently hardened with formaldehyde. A more promising method is to stretch the fiber in the presence of hardening agents (16, 20, 23, 30). For this purpose two conical stepped pulleys were installed (vertical pair in middle of panel, Figure 1). The lower conical pulley was partly immersed in a bath containing a heated solution of 30% sodium acetate and 5% formaldehyde, buffered to pH 5.8 with acetic acid (bath III, the same as that used throughout for final hardening of the fiber on the bobbin). With fifteen loops of the casein tow around the two conical pulleys, the fiber was simultaneously stretched and hardened by passage through the heated bath for approximately 2 minutes. This mechanism contributed 100% stretch, which absorbed some tendency of the fiber to sag under the heat treatment. A second stretching operation was imposed between the upper cone pulley and an adjacent godet wheel before the fiber was collected on the bobbin. (The set of conical pulleys on the left in Figure 1 was not used in these experiments.)

Table VA shows that these procedures increased the strength of the fiber containing aluminum salt from about 0.71 to 0.85 gram per denier. Other experiments showed that stretching the fiber in hot 20% sodium chloride increased the strength only slightly, while stretching in hot acetate buffer at pH 5.8 increased the strength moderately but not to the values obtained when formaldehyde was also present in the stretching bath. Contrary results were secured with fiber precipitated in the absence of aluminum salt (bath II). Stretching this fiber in a heated bath of acetate buffer and formaldehyde (Table VA), sodium chloride, or acetate buffer alone gave a weaker fiber.

TABLE IV. EFFECT OF DRAWOFF RATE AND GODET STRETCH ON FIBER STRENGTH

—A. Drawoff rate, m./min.	No Godet Stretch—Tensile strength (70° F., 65% r.h.), g./denier		—B. With Godet Stretch—Tensile strength (70° F., 65% r.h.), g./denier		
	Bath I	Bath II	Godet stretch, %	Bath I	Bath II
4.8	0.45	0.18	20	0.69	0.60
9.9	0.54	0.43	41	0.72	0.58
13.6	0.62	0.61	64	0.75	0.68
17.9	0.67	0.64	89	0.73	0.71
22.4	0.68	0.65	119	0.71	0.71
27.4	0.69	0.69	134	0.70	0.61
34.2	0.69	0.67	150	Tow breaks	
43.6	0.70	0.69			
47.0	Tow breaks				

\* Drawoff rate was 17.9 meters per min.

Since the presence of aluminum salt in the fiber proved so advantageous, fiber was stretched in a heated solution of 10% aluminum sulfate, 10% sodium sulfate, and 2% formaldehyde (bath IV). Fiber of even higher strength was obtained (Table VB). The best fiber of this series had a dry strength of 0.98 and wet strength of 0.46 gram per denier. Both the dry and wet breaking elongations were 52%. Immersed in water, the fiber increased in length by 6% but receded to its original length upon being dried and reconditioned. Boiling in water for 10 minutes produced a shrinkage of 19% measured on the wet fiber. It was not resistant to boiling in water for an hour unless it was acetylated.

lated (5, 7) or treated with quinone (12, 19). This fiber did not show arcing of the rings in the Debye-Scherrer x-ray photograph. However, when it was given a 50% stretch in clamps, a slight arcing of the inner ring was observed. The birefringence was positive and of magnitude  $5 \times 10^{-3}$ .

TABLE V. EFFECT OF STRETCH WITH PARTIAL HARDENING ON FIBER STRENGTH

Godelt Stretch <sup>a</sup> , %	Stretched in:	Tensile Strength <sup>b</sup> , G./Denier	
		Bath I	Bath II
A. EFFECT OF ALUMINUM SALT IN PRECIPITATING BATH <sup>c</sup>			
107	Air, 27° C.	0.72	0.74
127	Bath III, 27° C.	0.71	0.56
136	Bath III, 40° C.	0.77	0.69
173	Bath III, 50° C.	0.80	0.68
206	Bath III, 60° C.	0.85	0.65
B. EFFECT OF ALUMINUM SALT IN BOTH PRECIPITATING AND STRETCHING BATH <sup>d</sup>			
		Bath I	Bath I Wet tensile
255	Bath IV, 25° C.	0.77	0.24
349	Bath IV, 55° C.	0.81	0.28
349	Bath IV, 65° C.	0.92	0.34
472 <sup>e</sup>	Bath IV, 85° C.	0.98	0.46

<sup>a</sup> Maximum without breaking tow; the initial 100% of this stretch was obtained with the conical stepped pulleys.

<sup>b</sup> At 70° F. and 65% relative humidity.

<sup>c</sup> Drawoff rate, 17.9 meters per min.

<sup>d</sup> Drawoff rate, 16.6 meters per min.

<sup>e</sup> Pump rate was increased to 48 cc. and drawoff rate decreased to 15.2 meters per minute for this bobbin to make the higher stretch possible.

## DISCUSSION

In spinning casein fiber, it appears desirable within practical limits to seek mild conditions of alkalinity in the spinning solution and of acidity in the precipitating bath. Even if exposure to extreme conditions of pH does not entail injurious hydrolysis of the protein, excess acid or alkali in the fiber must eventually be neutralized and washed out. Otherwise the hydrophilic nature of salt groups formed in the protein or of inorganic salt present in the fiber heightens the absorption of water and its generally weakening effect. The spinning baths employed in the experiments described here resemble those used in the viscose rayon industry in their high acid and salt contents. While they operate acceptably, precipitation at higher pH values is possible (16).

The experiments on stretching are presented only to show the relative values of the particular procedures in producing stronger casein fibers. Any continuous process not involving final hardening of the fiber on the bobbin would doubtless yield different strength values. A marked increment in strength is induced by the stretching of fiber containing aluminum salt in hot buffered formaldehyde baths. The results suggest the trial of other combinations of mechanical and physical factors and of other salts such as those of chromium (10) and beryllium (27) in place of aluminum.

The properties of our best fiber do not provide a basis for anticipating the upper limits of dry and wet strengths, since the combined stretching and hardening treatment applied to this fiber was brief. Nevertheless, it is of interest to give some theoretical consideration to this point. The most plausible mechanism by which stretch becomes effective in increasing tensile strength is by orientation of micelles or of individual chains in the fiber. Maximum strength would appear to depend on chains of sufficient length, extension of chains parallel with the fiber axis, and packing of these chains. Casein of commerce is a globular protein with a low axial ratio, as shown by various properties including relatively low viscosity in dilute solution. If we assume a molecular weight for casein of 33,600 as determined by Burk and Greenberg (8), an average residue weight of 115, and a continuous chain of the amino acids present, there would be about 300 peptide links per molecule. Since the repeating peptide unit occupies a space of 3.5 Å., a fully extended chain would have a length of about 1000 Å. and a width of 10 Å. In a fiber the proper orienta-

tion of chains with an axial ratio of 100 should markedly increase the tensile strength. In view of these considerations the denaturation of casein and its treatment to obtain oriented protein chains is a promising line of research. Some common denaturing agents, such as urea, have been patented in this connection (4). However, our spinning experiments with urea solutions of casein have not thus far produced a fiber with any orientation detectable by x-ray diffraction or with an appreciably higher strength than is secured in fibers spun from sodium hydroxide solution. A number of procedures for the orientation of the peptide chains of casein have recently been investigated in this laboratory. It has been found that large extruded filaments of casein and other proteins can be converted by moisture, heat or a variety of chemical agents, and mechanical treatment to an oriented structure with chains extended along the fiber axis characteristic of silk and stretched wool (24, 25). The application of these findings to the production of oriented textile fiber by a continuous spinning process is now under investigation.

## ACKNOWLEDGMENT

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